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Technical Report 2

**EPITAXIAL GROWTH AND STRUCTURE OF HIGHLY
MISMATCHED OXIDE FILMS WITH
ROCK-SALT STRUCTURE ON MgO**

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EPITAXIAL GROWTH AND STRUCTURE OF HIGHLY MISMATCHED OXIDE FILMS WITH ROCK-SALT STRUCTURE ON MgO

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ABSTRACT

CaO thin films were grown on (001) MgO single crystal substrates by a chemical solution deposition method to study the influence of a relatively high lattice mismatch (14%) on the epitaxial growth. In order to minimize an influence of a different crystal structure and chemistry between film and substrate, film and substrate were chosen to have the same structure (NaCl) and a similar chemistry. The films were heat treated until they broke up into single crystal islands on the MgO substrate. X-ray pole figure analysis and TEM observations of the CaO-films showed that most of the grains had a single out-of-plane orientation (111)CaO \parallel (001)MgO, corresponding to two non-redundant, symmetry related in-plane variants $[1;\bar{1}0](111)\text{CaO} \parallel [110](001)\text{MgO}$ and $[1;\bar{1}0](111)\text{CaO} \parallel [\bar{1};10](001)\text{MgO}$. A $\Sigma 7/\Sigma 8$ Near Coincidence Site Lattice (NCSL) model could be constructed for the interface, that suggests good lattice and charge matching for the observed orientation relations. The mechanisms and energetics leading to the experimentally observed orientation relations are discussed.

INTRODUCTION

It is well known, that in thin films, a large fraction of the differential strain and thus, strain energy due to lattice mismatch can be accommodated by a network of misfit dislocations at or near the interface between the two materials [1]. Other orientation relationships than the "cube-on-cube" orientation relationship ($[100](001)_f \parallel [100](001)_s$) are generally observed when ϵ_s is larger than approximately 10-15% [1, 2]. It is assumed that these orientations have a lower interfacial energy. Except for the study of Takayanagi et al. [3], no former study in the field of epitaxy systematically varies ϵ_s to greater than a few percent. In their study; however, in addition to the influence of the lattice mismatch, differences in chemistry and structure of film and substrate can lead to a different growth orientation relation. In order to minimize this influence; in our study, films and substrates were chosen to have the same crystal structure (rock-salt) and similar chemistry (oxides). The series of oxides includes NiO (lattice parameter: $a \approx 0.4177\text{nm}$), MgO (0.4213nm), CoO (0.4258nm), FeO (0.4307nm), MnO (0.445nm), CdO (0.4695nm), CaO (0.4811nm), SrO (0.5160nm) and BaO (0.5539nm) [4]. When MgO is the substrate, the lattice mismatch strain, ϵ_s , at room temperature is in the range between -0.9% (NiO) and 31.5% (BaO). The chemical solution deposition method was employed for thin film preparation [5], because of its simplicity and because none of the former studies involving this method systematically varies the lattice mismatch above $\approx 2\%$. Investigations of perovskite films have shown, that high quality epitaxial films with semicoherent interfaces can be obtained by the chemical solution deposition method [6].

Vaidya et al. showed already, that NiO-films could be grown on MgO with the orientation relation $[100](001)_f \parallel [100](001)_s$ [7] as expected, because the lattice mismatch is relatively small. Because of different types of instabilities, other chemistries within the chosen model system are much more difficult to prepare. For example, FeO and MnO require extremely low oxygen partial pressures [8] whereas CdO is volatile at temperatures required to form epitaxial films [9]. CaO, SrO and BaO readily form carbonates due to reactions with CO_2 within the atmosphere [8,10] during furnace cooling. In addition, CaO, SrO and BaO easily form

hydroxides when brought into contact with water [11]. These reactions made the preparation and investigation of specimens very difficult, in some cases even impossible.

In the following, the preparation and characterization of CaO-films (14.2%) is described with observations that include structural characterization by X-ray diffraction (XRD), scanning electron microscopy (SEM) and conventional transmission electron microscopy (TEM) at plan-view samples.

EXPERIMENT

Thin films of CaO were prepared by spin-coating (001)-oriented MgO-substrates with a metalorganic precursor solution of Ca 2-ethylhexanoate (STREM Chemicals, Newburyport, MA, USA) in toluene. The rotation speed during spin-coating was $\approx 10\,000$ rpm. Prior to spin-coating, the MgO substrates were cleaved in air from a single crystal (Kristallhandel Kelpin, Leimen, Germany). It is known from literature [5] and confirmed by thermogravimetric analysis (TGA), that pyrolysis of the Ca-precursor doesn't lead directly to an oxide, but to a carbonate. TGA (Netzsch STA 409) in air showed, that the conversion temperature from the carbonate to the oxide is $\approx 800^\circ\text{C}$. Therefore, relatively high heating temperatures have been used (1400°C) to produce the oxide. In addition, because CaO readily forms carbonates in air, films have been sputter-coated with Au or AuPd immediately after deposition. The protective coating also prevents the films from reacting with water [11] during the preparation of TEM plan-view specimens. TEM plan-view specimens were prepared by polishing, dimpling and ion-milling with Ar-ions from the substrate side (Gatan Duo Mill).

The characterization of structure and morphology was carried out using XRD (Siemens D5000, Siemens D500, Scintag XDS 2000), X-ray texture analysis (Siemens D500 with Eulerian cradle from Huber), SEM (JEOL, JSM 6400), and conventional TEM (JEM 2000FX, JEOL).

RESULTS

XRD (θ - 2θ)-measurements of CaO-films heat treated at 1400°C (Fig. 1) revealed that (111)CaO \parallel (001)MgO was the dominant out-of-plane orientation of the CaO film on MgO. X-ray pole figure analysis [12] indicated, that the preferred growth orientations are two non-redundant symmetry related in-plane variants of (111)CaO \parallel (001)MgO: $[1; \bar{1}0](111)\text{CaO} \parallel [110](001)\text{MgO}$ and $[1; \bar{1}0](111)\text{CaO} \parallel [\bar{1}; 10](001)\text{MgO}$. Figure 2 shows that the CaO film is composed of islands.

TEM plan-view specimens revealed that the islands were single crystals. In addition, selected area diffraction (SAD) confirmed that the single crystalline islands have the orientation relationship determined by XRD [12].

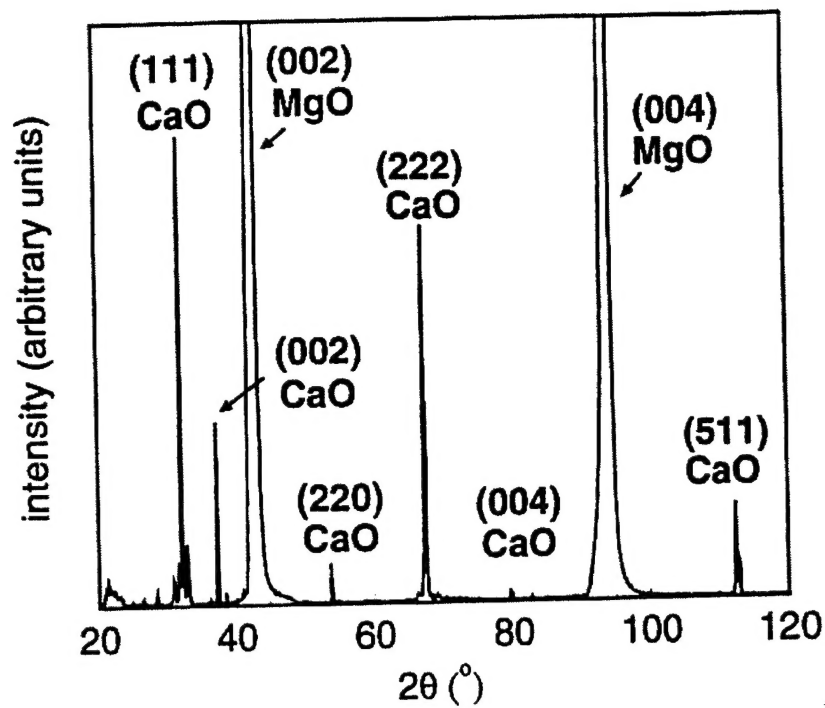


Fig. 1 XRD (θ - 2θ)-measurements of a CaO-film on MgO heat treated at 1400°C. The preferred out-of-plane orientation of the film is (111)CaO \parallel (001)MgO. In addition, other orientations of CaO ((220), (511)) are also detected.

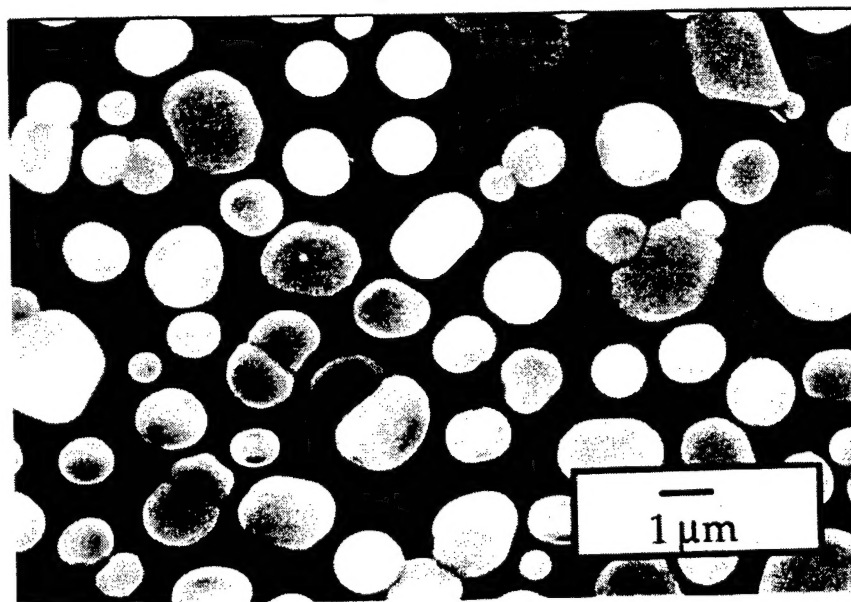


Fig. 2 SEM micrograph of a CaO-film on MgO. The film consists of islands.

DISCUSSION

The experimental results have shown, that after the heat treatment, mainly epitaxial single crystal grains with the out-of-plane orientation of (111)CaO || (001)MgO are present. According to the structure and morphology observed, it is very likely that the epitaxial film grains have undergone abnormal grain growth concurrent with a morphological instability, as described by Miller et al. [13]. The grains that undergo abnormal grain growth in a columnar microstructure are those with the lowest energy, which is given by the sum of surface and interface energy $\gamma_s + \gamma_i$ [14]. As the {100}CaO-surface has a lower surface energy than the {111}CaO-surface ($\gamma_{s,\{111\}} \approx 1.9 \text{ J/m}^2$ [15] and $\gamma_{s,\{100\}} \approx 0.8 \text{ J/m}^2$ [16]), it is suggested, that a lower interfacial energy γ_i is the driving force for the growth of the observed epitaxial orientations.

As shown in Fig. 3, a geometrical $\Sigma 7/\Sigma 8$ near coincident site lattice (NCSL)-model is proposed to be consistent with the observed orientation relations. The (111)-planes of CaO consist alternating of planes of Ca^{2+} - and O^{2-} -ions. Therefore, the ending plane of the film at the interface (terminating plane) also can consist either of Ca^{2+} - or of O^{2-} -ions. In Fig. 3, the case of Ca^{2+} -termination is shown. In principle, other translations of the CaO with regard to the MgO would be possible. However, it is assumed, that the NCSL-sites are electroneutral. A model for O^{2-} -termination can be derived by exchanging the Mg^{2+} - and O^{2-} -ions in MgO. The mismatch at room temperature for the 7:8 coincidence along $[110]\text{MgO}$ and $[1\bar{1}10]\text{CaO}$ is just $F_{s,1} \approx -0.1\%$. In the orthogonal direction, ion rows of opposite charge are parallel with a mismatch of $F_{s,2} \approx 1.1\%$. Thermal expansion mismatch can be neglected ($\approx 0.1\%$ between room temperature and 1400°C [17]).

The same orientation has been observed before at other systems with similar lattice mismatches ($\approx 13\text{--}18\%$, for example Ag on Ni [18]). The important difference between our study and the metal-systems is, that in the ionic system CaO on MgO, in addition, coincidences of ions with the same charge have to be avoided.

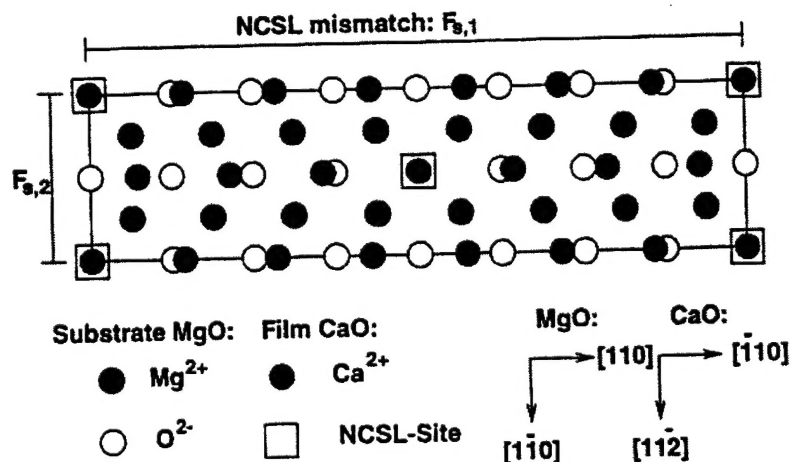


Fig. 3 $\Sigma 7 / \Sigma 8$ NCSL-model (referred to CaO / MgO) of the interface between CaO and MgO (one variant). $\langle 110 \rangle$ -ion rows of opposite charge are parallel with a mismatch of 1.1%

CONCLUSION

The epitaxial orientation relations determined for CaO on MgO show, that for high lattice mismatches (>10%) NCSL-orientations can occur. From the growth mechanisms proposed, it is concluded, that the driving force for the formation of these orientations is their lower interfacial energy compared to epitaxial growth with the orientation relationship $[100](001)$ film $\parallel [100](001)$ substrate.

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